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A SIMPLIFIED EQUILIBRIUM HYDROCARBON-AIR COMBUSTION

GAS MODEL FOR CONVENIENT USE IN AIR-BREATHING

ENGINE CYCLE COMPUTER PROGRAMS

A Thesis

Presented to

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Master of Aerospace Engineering

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by

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ABSTRACT

A simplified hydrocarbon-air combustion gas model, including the effects of dissociation, for convenient use in engine cycle computer programs is presented. The gene-alized model reduces to the hydrogen-air system as well as dissociating air. The exclusion of chemical species containing atomic nitrogen allows a considerable simplification of the composition equations. The thermodynamic properties of stoichiometric combustion of the kerosene-air and hydrogen-air systems are computed with the simplified model and compared with more comprehensive gas models. In addition, the effect of the neglected chemicals species on the performance of a idealized subsonic combustion ramjet is presented. The simplified gas model has been used to define the limiting conditions for solid carbon and ammonia formation for fuel rich gas mixtures. A computer program listing of the simplified gas model calculation procedure is presented.

ACKNOWLEDGMENTS

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SYMBOLS AND NOTATION

F_{net}	net thrust, lbf
f	fuel-air ratio
f_s	stoichiometric fuel-air ratio
g	acceleration due to gravitational field of the earth, 32.174 ft/sec^2
$\dfrac{G}{RT}$	Gibbs free energy
H	enthalpy, Btu/lbm
I_{sp}	specific impulse, sec
J	mechanical equivalent of heat, 778.2 ft-lbf/Btu
K	equilibrium constant in terms of partial pressures
M	molecular weight
n	ratio of hydrogen atom to carbon atom in fuel molecule
p	pressure, atmospheres
q	dynamic pressure, lbf/ft^2
R	universal gas constant, 1.98588 Btu/mole-$^{\circ}$R
R_{ch}	ratio of carbon to hydrogen atoms in fuel molecule, $\dfrac{1}{n}$
R_{eq}	equivalence ratio, $\dfrac{f}{f_s}$
S	entropy, Btu/lbm-$^{\circ}$R
T	temperature, $^{\circ}$R
V	velocity, ft/sec
W_A	airflow rate, lbf/sec
X	mole fraction

Subscripts

∞ free-stream conditions

J Jth species

j jet

lim   limiting condition for solid carbon or ammonia formation

s   static conditions

t   stagnation conditions

Superscripts

$^\circ$ at reference pressure, 1 atmosphere

CHAPTER I

INTRODUCTION

Recent and continuing advances in fluid dynamics and metallurgy have opened new domains of power and efficiency to the air-breathing combustion engine. The combined effect of technological advances and the demand for greater operating flexibility in the aircraft power plants have led to certain design trends which are significant from a thermodynamic standpoint, namely: the maximum allowable internal temperatures, pressures, and gas stream velocities are increasing, and minimum internal operating pressures are decreasing as well.

Developments in the area of compressor and turbine blade cooling have been instrumental in extending the potential range of efficient operation of the turbojet engine to high supersonic Mach numbers and high altitudes. As discussed in Zucrow (Ref. 1), for turbojets employing uncooled turbine blades, the temperature of the gases leaving the combustion chambers must be limited to approximately 2000° R due to stress, creep, and stress duration considerations. Because of that temperature limitation the overall fuel-air ratio for a turbojet engine burning a hydrocarbon fuel, such as JP-4 (CH_2), is quite low, of the order of 0.015 ($R_{eq} \approx 0.25$). Current turbojet designs, such as those proposed for the supersonic transport, employ turbine blade cooling which permits turbine inlet temperatures of approximately 2800° R (Rothrock, Ref. 2) and results in fuel-air ratios of the order of 0.03 ($R_{eq} \approx 0.5$). Advanced turbojet engines which employ hydrogen for both

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fuel and turbine cooling are being studied with stoichiometric combustion and resulting turbine inlet temperatures of approximately 4000° R.

The ramjet engine is better suited for propulsion problems requiring high flight speeds. No such temperature limitation is applicable to the ramjet engine because it has no moving parts that are subjected simultaneously to dynamic loads and high temperatures. Consequently, stoichiometric combustion of high energy fuels, such as methane (CH_4) and hydrogen, may be utilized for the ramjet engine. In addition, the high stagnation temperatures attained by the air at high flight Mach numbers result in combustion temperatures approaching 5000° R for stoichiometric methane combustion and 6500° R for stoichiometric hydrogen combustion.

As discussed by Ferri (Ref. 3), the concept of the supersonic combustion ramjet appears attractive for very high Mach numbers and altitudes approaching orbital conditions. Since the fuel is mixed and ignited in a supersonic airstream, internal temperatures would not exceed 5000° R (stoichiometric hydrogen-air combustion), even at flight Mach numbers of the order of 12. Because of the application of the supersonic combustion ramjet to high altitude flight and the fact that a large portion of the energy in the airstream remains in the form of kinetic energy, internal operating pressures can be substantially below sea level atmospheric pressure.

An accurate knowledge of the thermodynamic properties and behavior of these engine's working fluid under all operating conditions is a basic requirement for effective design. However, at high temperatures

and low pressures, considerable difficulties arise in calculating the
thermodynamic properties of combustion gas mixtures - difficulties which
stem from the phenomena of internal energy excitation coupled with
chemical dissociation.

In the past, methods such as presented by Hall and Weber in
Reference 4 have been used to calculate the thermodynamic properties of
combustion gases for air-breathing engine cycle computations. The method
of Reference 4 is based on separate calculations of thermodynamic
properties of air and the products of combustion of a stoichiometric
fuel-air mixture. It is assumed that the properties of the combustion
products for any fuel-air ratio less than stoichiometric may be obtained
by linear interpolation between the two extreme cases. Results of this
method are exact for cases with no dissociation. However, when disso-
ciation is taken into account, errors arise because the method does not
account for the change in composition of the gases when they are mixed.
This error is small for turbojet or turbofan calculations since tempera-
tures are relatively low and dissociation is not extensive. However,
the high operating temperatures of hypersonic engine cycles may result
in cases of extreme dissociation and cause large errors in calculating
engine performance.

The method of Reference 4 does not allow engine calculations for
equivalence ratios greater than unity. However, at high Mach number
flight, the fuel required to cool aerodynamic surfaces and engine
component may force engine operation into this region.

In short, the method of Reference 4 does not provide a sufficiently general basis for engine cycle calculations under all conditions of current and future interest.

Chemical equilibrium theory which governs dissociation phenomena has long been formulated, for example by Clarke and McChesney (Ref. 5). However, its application to complex combustion gas mixtures has proven so tedious and complicated as to preclude direct use in engine cycle computer programs. The General Electric combustion gas models of References 6 and 7, which serve as a basis of comparison for the simplified gas model presented herein, are elaborate treatments of the hydrogen-air and kerosene-air systems.

The generalized hydrogen-air model of Reference 6 assumes 12 chemical species, requiring eight independent chemical reactions leading to eight equilibrium expressions. Since the initial proportions of hydrogen and air define four mass balance equations, the mathematical solution: 12 equations - 12 unknowns, is demonstrated. The reduction of the system of equations to one equation - one unknown, as recommended by Erickson, Kemper, and Allison in Reference 8 - is extremely tedious. With the exclusion of the technique of Reference 8, hope for the solution of this system by a single level iteration is abandoned. The adoption of a two-level iteration or one of the methods summarized by Zeleznik and Gordon in Reference 9 to solve for gas composition has a great effect on the utility of the computation procedure as a subroutine for an engine cycle computer program. Consequently, the most efficient means of representing the thermodynamic properties of these gas models

in an engine cycle program is by an elaborate system of fitted curves, sacrificing both computer storage and accuracy.

The purpose of the simplified gas model presented herein is to incorporate the substantial effects of dissociation consistent with convenient use in computerized engine cycle calculations. The proposed gas model is simplified in the sense that the formation of species containing atomic nitrogen is neglected. This assumption enables the solution for chemical composition to be obtained with a single level iteration. Although the original intent of this study was directed toward the hydrogen-air system, it was found that the model could be generalized to any hydrocarbon-air system, as well as dissociating air, with little additional complexity. The computer program included can be readily incorporated as a subroutine in an engine cycle program or used alone to generate Mollier diagrams. Inputs to the program are the ratio of carbon atoms to hydrogen atoms in the fuel molecule, equivalence ratio, temperature, and pressure. Outputs from the program are the mole fractions of the chemical species assumed, enthalpy, entropy, and molecular weight.

CHAPTER II

ANALYSIS

Description of Gas Model

The range of temperatures and pressures of interest for air-
breathing engine application is assumed to be below temperatures of
7000° R and between pressures of 0.001 and 100 atmospheres. In this
range of conditions, References 3 and 4 indicate that the formation of
nitrogen species, such as N, NH, NH_3, and NO occurs in negligible
amounts and, therefore, has a very small effect on the thermodynamic
properties of combustion gas mixtures. The assumption to neglect these
species has a great effect on the complexity of the calculation
procedure since molecular nitrogen can be considered inert. The effect
of this assumption on the thermodynamic properties of gas mixtures and
on the performance of an idealized ramjet engine will be discussed in
the section entitled Results and Discussion.

Figure 1 is a diagram illustrating the chemical species and
required chemical reactions considered in this gas model. The figure
is divided into regions of temperature and equivalence ratio. Above
$T_{cut-off}$ the gas is considered to be dissociating. The chemical
species assumed for pure air ($R_{eq} = 0$) are identical to those of
Reference 6 and include atomic nitrogen species. For the combustion
gas model ($R_{eq} > 0$) the dissociated nitrogen species (N, NH, NH_3, NO)
are not included. It is apparent that by excluding the species and
reaction containing carbon, the model reduces to the hydrogen-air system.

Species

O₂, N₂, Ar, O, NO, N → O_2, N_2, Ar, O, NO, N

Reactions

$2O = O_2$
$2N = N_2$
$N + O = NO$

Species

$H_2O, CO_2, O_2, H_2, N_2, Ar, O, H, OH, CO$

Reactions

$2H + O = H_2O$ $2H = H_2$
$CO + O = CO_2$ $2O = O_2$
                  $O + H = OH$

$T_{cut\text{-}off} = 100 \log_{10} P + 2800$

Species

O_2, N_2, Ar

Species

O_2, N_2, Ar, H_2O, CO_2

Species

N_2, Ar, H_2O, CO_2

Species

$N_2, H_2, Ar, H_2O, CO_2, CO$

Reactions

$H_2 + CO_2 = CO + H_2O$

$R_{eq} = 0$ $0 < R_{eq} < 1$ $R_{eq} = 1$ $R_{eq} > 1$

Equivalence ratio

Dissociating ← | → Nondissociating

Temperature

Figure 1.- Description of gas model.

Below $T_{cut-off}$, in general, all chemical reactions are complete and combustion products completely formed. Therefore, the initial proportions of elements are sufficient to define the gas composition. However, for $R_{eq} > 1$, the gas model of Reference 7 indicates that CO may form even below $T_{cut-off}$. As a result, the initial proportions of elements are not sufficient to define the gas composition and one chemical reaction is required.

In the region of fuel rich operation, solid carbon and ammonia may form. The limiting pressure for the formation of solid carbon depends upon the relative proportions of carbon dioxide (CO_2) and carbon monoxide (CO), equivalence ratio, and temperature. However, there is a limiting equivalence ratio for a given hydrocarbon-air system above which carbon will form under any condition of pressure and temperature.

The formation of ammonia was considered only for the hydrogen-air case since the formation of solid carbon preceded the formation of ammonia for the combustion products of all the hydrocarbon-air systems studied. The limiting pressure for the formation of a given amount of ammonia depends upon the relative proportion of nitrogen (N_2) and hydrogen (H_2), equivalence ratio, and temperature.
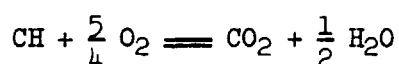
It should be emphasized that the combustion gas model, including the criteria for solid carbon and ammonia formation, is based entirely upon equilibrium theory of gases.

Derivation of Gas Model

The general equations presented in this section for computing chemical composition and combustion gas properties make use of the

following assumptions: (1) the formulated gas mixtures simulate the products of complete, constant pressure, adiabatic combustion; (2) the gas mixtures are in thermal and chemical equilibrium; (3) the ideal gas equation of state is valid; (4) only gas phases are considered; and (5) the effects of ionization are negligible.

Overall stoichiometry and gas model constants.- In order that the simplified gas model may apply to the combustion of any hydrocarbon fuel a generalized statement concerning the atomic composition of the fuel is required. Consider the following stoichiometric reactions:

$$CH + \frac{5}{4} O_2 = CO_2 + \frac{1}{2} H_2O$$

$$CH_2 + \frac{6}{4} O_2 = CO_2 + \frac{2}{2} H_2O$$

$$CH_3 + \frac{7}{4} O_2 = CO_2 + \frac{3}{2} H_2O$$

$$CH_4 + \frac{8}{4} O_2 = CO_2 + \frac{4}{2} H_2O$$

In general terms:

$$CH_n + \frac{n + 4}{4} O_2 = CO_2 + \frac{n}{2} H_2O$$
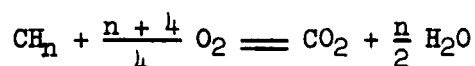
where

$$n = \frac{\text{no. atoms H}}{\text{no. atoms C}} \text{ in fuel molecule}$$

Thus, in the general case:

$$\frac{\text{no. moles } CH_n}{\text{no. moles } O_2} = \frac{4R_{eq}}{n + 4}$$

where R_{eq} is the equivalence ratio. The initial composition of air incorporated in this gas model is the same as that of Reference 6; that is, combustion is assumed to have occurred with dry air of the following composition by volume:

O_2	N_2	A
20.9495 per cent	78.0881 per cent	0.9624 per cent

The following constants and parameters define, in general terms, the initial atomic proportions of the elements in the gas mixture.

$$C_1 = \frac{\text{no. atoms A}}{\text{no. atoms N}} = 0.00616227$$

$$C_2 = \frac{\text{no. atoms N}}{\text{no. atoms O}} = 3.727445$$

$$C_3 = \frac{\text{no. atoms C}}{\text{no. atoms O}} = \frac{2R_{eq}}{n + 4}$$

$$C_4 = \frac{\text{no. atoms H}}{\text{no. atoms O}} = \frac{2nR_{eq}}{n + 4}$$

Defining $R_{ch} = \frac{1}{n}$, then

$$C_3 = \frac{2R_{eq}R_{ch}}{1 + 4R_{ch}}$$

$$C_4 = \frac{2R_{eq}}{1 + 4R_{ch}}$$

For the special case of hydrogen-air combustion:

$$2H_2 + O_2 \rightleftharpoons 2H_2O$$
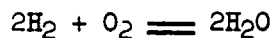
$$\frac{\text{no. moles } H_2}{\text{no. moles } O_2} = 2R_{eq}$$

$$R_{ch} = 0 \qquad\qquad C_3 = 0 \qquad\qquad C = 2R_{eq}$$

The stoichiometric fuel-air ratio is given by:

$$f_s = 0.028931 \left[\frac{1.008 + 12.01R_{ch}}{1 + 4R_{ch}} \right]$$

It is of value to represent the equilibrium constants for the assumed reactions in a convenient manner. The treatment of chemical equilibria in Reference 5 leads to the equilibrium expression for a general reaction:

$$aA + bB \rightleftharpoons cC + dD$$

The equilibrium expression is:

$$\frac{x_C^c x_D^d}{x_A^a x_B^b} = P^{-(c+d-a-b)} \cdot K$$

where

$$K = \exp\left[-\left\{ c\,\frac{G_C^o}{RT} + d\,\frac{G_D^o}{RT} - a\,\frac{G_A^o}{RT} - b\,\frac{G_B^o}{RT} \right\} \right]$$

Figure 2 shows the variation of $\log_{10} K$ with $\frac{1}{T}$ for the chemical reactions considered in this gas model. The values of Gibbs free energy $\frac{G_j^o}{RT}$ for the species were taken from the data tabulations in References 6 and 7. Figure 2 indicates that the equilibrium constants can be represented as linear functions.

Hydrocarbon-air gas model with dissociation.- The following gas model applies to the region:

$$T > T_{cut\text{-}off}, \quad R_{eq} > 0$$

Chemical species assumed:

$$H_2O, \quad CO_2, \quad O_2, \quad H_2, \quad N_2, \quad A, \quad O, \quad H, \quad CO, \quad OH$$

Chemical reactions:

$$2H + O = H_2O, \quad 2H = H_2, \quad 2O = O_2, \quad O + CO = CO_2, \quad H + O = OH$$
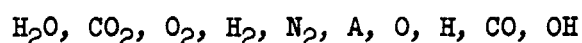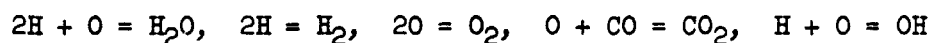
Mass conservation equations:

$$\sum_{J=1}^{10} X_J = 1 \tag{1}$$

$$X_A = C_1(2X_{N_2}) \tag{2}$$

$$2X_{N_2} = C_2(2X_{CO_2} + X_{CO} + X_{H_2O} + 2X_{O_2} + X_O + X_{OH}) \tag{3}$$
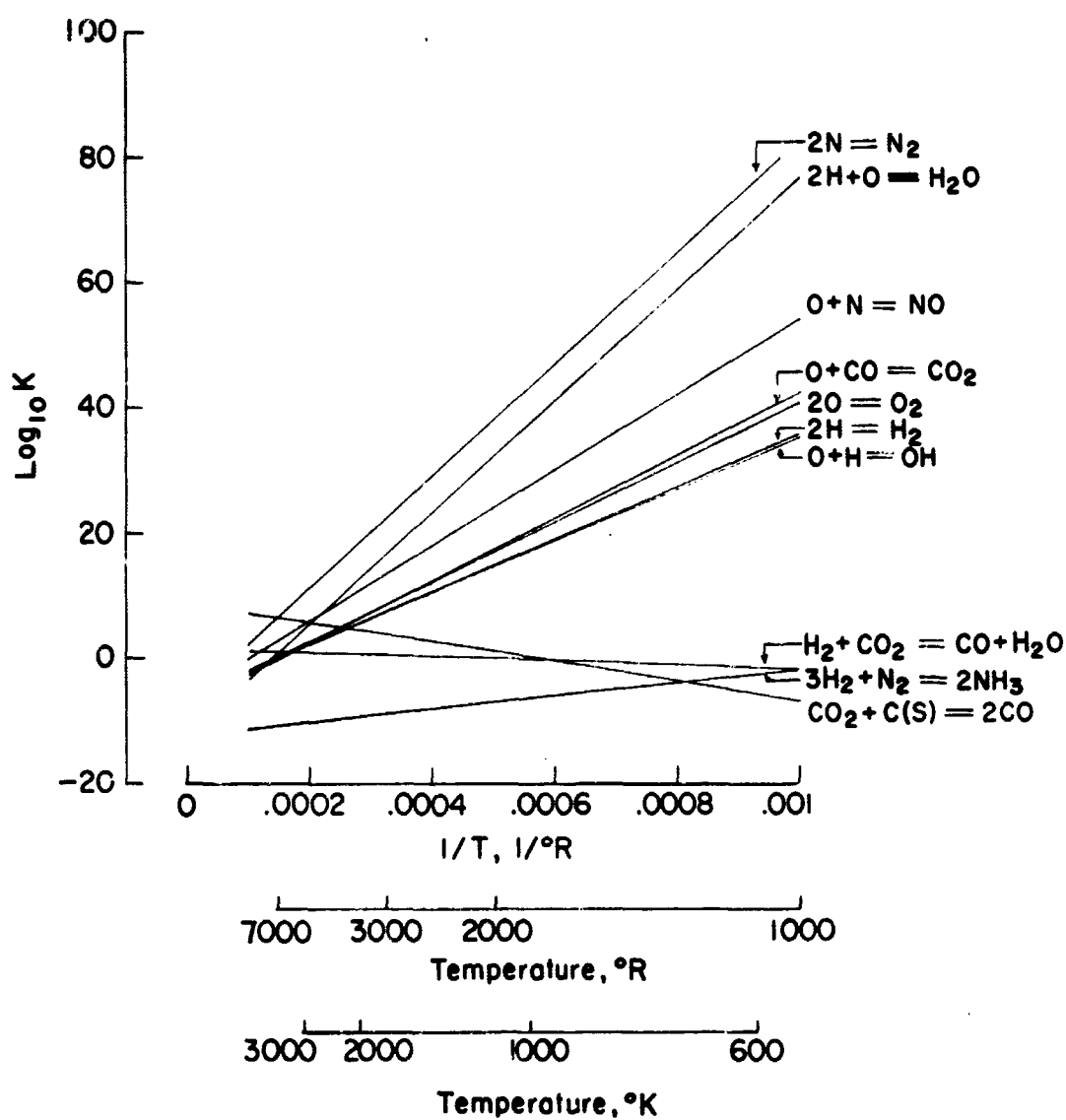
Figure 2.- Variation of equilibrium constants with temperature for gas
model reactions.

$$X_{CO_2} + X_{CO} = C_3(2X_{CO_2} + X_{CO} + X_{H_2O} + 2X_{O_2} + X_O + X_{OH}) \qquad (4)$$

$$X_H + 2X_{H_2} + 2X_{H_2O} + X_{OH} = C_4(2X_{CO_2} + X_{CO} + X_{H_2O} + X_O + X_{OH} + 2X_{O_2})$$

$$(5)$$

Equilibrium expressions:

$$X_{H_2O} = P^2K_1X_OX_H^2 \qquad (6)$$

$$X_{H_2} = PK_2X_H^2 \qquad (7)$$

$$X_{O_2} = PK_3X_O^2 \qquad (8)$$

$$X_{CO_2} = PK_4X_OX_{CO} \qquad (9)$$

$$X_{OH} = PK_5X_OX_H \qquad (10)$$

Solving for two equations - two unknowns in X_O, X_H:

$$\alpha = \left\{ A_{22}X_O^2 + A_{21}X_O + A_{20} \right\}X_H^2 + \left\{ A_{12}X_O^2 + A_{11}X_O + A_{10} \right\}X_H$$

$$+ \left\{ A_{03}X_O^3 + A_{02}X_O^2 + A_{01}X_O + A_{00} \right\} = 0$$

$$\beta = \left(B_{22}X_0^2 + B_{21}X_0 + B_{20} \right) X_H^2 + \left(B_{12}X_0^2 + B_{11}X_0 + B_{10} \right) X_H$$

$$- \left(B_{03}X_0^3 + B_{02}X_0^2 + B_{01}X_0 \right) = 0$$

For $R_{eq} > 1$ the iteration function, α, is insensitive to changes in X_0. As a result, X_H is used as the iteration variable in this region of computation. Unfortunately, if X_H is assumed, the expression β is cubic in X_0 and an additional iteration is required. For fuel rich hydrogen-air mixtures $B_{03} = 0$, β is quadratic in X_0, and the single level iteration is maintained. However, for fuel rich mixtures containing carbon, a double level iteration is necessary for solution, where

$$A_{22} = P^3 K_1 K_4 (1 - 2C_3 + C)$$

$$A_{21} = P^2 \left\{ K_1 (1 + C) + 2K_2 K_4 (1 - 2C_3) \right\}$$

$$A_{20} = 2PK_2 (1 - C_3)$$

$$A_{12} = P^2 K_4 K_5 (1 - 2C_3 + C)$$

$$A_{11} = P \left\{ K_5 (1 + C) + 2K_4 (1 - 2C_3) \right\}$$

$$A_{10} = 2(1 - C_3)$$

$$A_{03} = 2CP^2 K_3 K_4$$

$$A_{02} = P \left\{ 2K_3 (C + C_3) + K_4 (1 - 2C_3 + C) \right\}$$

$$A_{01} = 1 + C - 2PK_4(1 - 2C_3)$$

$$A_{00} = -2(1 - C_3)$$

and

$$B_{22} = P^3 K_1 K_4 \left\{ 2(1 - C_3) - C_4 \right\}$$

$$B_{21} = P^2 \left\{ K_1 \left[2(1 - C_3) - C_4 \right] + 2K_2 K_4 (1 - 2C_3) \right\}$$

$$B_{20} = 2PK_2(1 - C_3)$$

$$B_{12} = P^2 K_4 K_5 (1 - 2C_3 - C_4)$$

$$B_{11} = P \left\{ K_5(1 - C_3 - C_4) + K_4(1 - 2C_3) \right\}$$

$$B_{10} = 1 - C_3$$

$$B_{03} = 2C_4 P^2 K_3 K_4$$

$$B_{02} = C_4 P \left\{ 2K_3 + K_4 \right\}$$

$$B_{01} = C_4$$

$$C = 1 + C_2(1 + 2C_1)$$

Setting C_3 and K_4 equal to zero reduces the system to identically the hydrogen-air case. The expressions for α and β are satisfied simultaneously by use of the Newton Iteration Scheme. Newton's iteration scheme for determining X_0 and X_H can be written as

$$X_0(L + 1) = X_0(L) - \frac{\alpha(X_0(L), X_H(L))}{\frac{d}{dX_0}(\alpha(X_0(L), X_H(L)))}$$

Where $X_0(L)$ is the Lth approximation of X_0 and the derivative of $\alpha(X_0, X_H)$ with respect to X_0 is

$$\frac{d\alpha}{dX_0} = \frac{\partial\alpha}{\partial X_0} - \frac{\partial\alpha}{\partial X_H}\left[\frac{\frac{\partial\beta}{\partial X_0}}{\frac{\partial\beta}{\partial X_H}}\right]$$
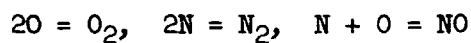
<u>Air-gas model with dissociation.</u>- The following gas model applies to the region:

$$T > T_{cut-off}, \quad R_{eq} = 0$$

Chemical species assumed:

$$O_2, \quad N_2, \quad A, \quad O, \quad NO, \quad N$$

Reactions:

$$2O = O_2, \quad 2N = N_2, \quad N + O = NO$$

Mass conservation equations

$$\sum_{J=1}^{6} X_J = 1 \tag{1}$$

$$X_A = C_1(2X_{N_2} + X_{NO} + X_N) \tag{2}$$

$$2X_{N_2} + X_{NO} + X_N = C_2(2X_{O_2} + X_O + X_{NO}) \tag{3}$$

Equilibrium expressions

$$X_{O_2} = PK_3 X_O^2 \tag{4}$$

$$X_{N_2} = PK_6 X_N^2 \tag{5}$$

$$X_{NO} = PK_7 X_O X_N \tag{6}$$

Solving for two equations two unknowns in X_O, X_N:

$$\alpha = A_{20}X_N^2 + \left\{A_{11}X_O + A_{10}\right\}X_N + \left\{A_{02}X_O^2 + A_{01}X_O + A_{00}\right\} = 0$$

$$\beta = B_{20}X_N^2 + \left\{B_{11}X_O + B_{10}\right\}X_N - \left\{B_{02}X_O^2 + B_{01}X_O\right\} = 0$$

where

$$A_{20} = (1 + 2C_1)PK_6 \qquad\qquad B_{20} = 2PK_6$$

$$A_{11} = (1 + C_1)PK_7 \qquad\qquad B_{11} = (1 - C_2)PK_7$$

$$A_{10} = 1 + C_1 \qquad\qquad B_{10} = 1$$

$$A_{02} = PK_3 \qquad\qquad B_{02} = 2C_2PK_3$$

$$A_{01} = 1 \qquad\qquad B_{01} = C_2$$

$$A_{00} = -1$$

The simultaneous solution of α and β is subject to the same iteration procedure as the gas model of the previous section.

Fuel rich gas model with solid carbon formation.- The following gas model applies to the region:

$$T \leq T_{\text{cut-off}}, \quad R_{\text{eq}} > 1$$

Chemical species assumed:
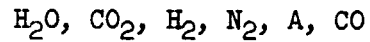
$$H_2O, \; CO_2, \; H_2, \; N_2, \; A, \; CO$$

Chemical reactions:

$$H_2 + CO_2 = CO + H_2O$$
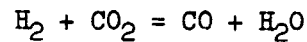
Mass conservation equations:

$$\sum_{J=1}^{6} X_J = 1 \tag{1}$$

$$X_A = C_1(2X_{N_2}) \tag{2}$$

$$2X_{N_2} = C_2(2X_{CO_2} + X_{CO} + X_{H_2O}) \tag{3}$$

$$X_{CO_2} + X_{CO} = C_3(2X_{CO_2} + X_{CO} + X_{H_2O}) \tag{4}$$

$$2X_{H_2} + 2X_{H_2O} = C_4(2X_{CO_2} + X_{CO} + X_{H_2O}) \tag{5}$$

Equilibrium expressions:

$$X_{H_2O}X_{CO} = K_8 X_{H_2} X_{CO_2} \tag{6}$$

Solving for X_{CO} yields:

$$AAX_{CO}^2 + BBX_{CO} + CC = 0$$

where .

$$AA = (1 - K_8)(C + C_4 + 2C_3 - 1)^2$$

$$BB = (C + C_4 + 2C_3 - 1)\left[2(1 - 2C_3) + K_8(C_4 + 6C_3 - 2)\right]$$

$$CC = 2C_3 K_8 (2 - C_4 - 4C_3)$$

Consider the following reaction:

$$CO_2 + C(S) = 2CO$$
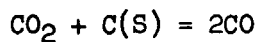
Equilibrium expression:

$$P_{lim} = \frac{K_9 X_{CO_2}}{X_{CO}^2}$$

If $P > P_{lim}$, solid carbon will form. There is, however, an equivalence ratio for the combustion products of a given hydrocarbon (R_{ch}), where solid carbon will form even in a vacuum.

Consider the equilibrium expression:

$$P_{lim}X_{CO}^2 = K_9 X_{CO_2}$$

$$P_{lim} \rightarrow 0, \quad X_{CO_2} \rightarrow 0$$

Setting $X_{CO_2} = 0$ in the system last derived, gives:

$$R_{eq,lim} = \frac{1 + 4R_{ch}}{2R_{ch}}$$

Nondissociating gas model.- The following gas model applies to the region:

$$T \leq T_{cut\text{-}off}$$

Chemical species assumed:

$$H_2O, \quad CO_2, \quad O_2, \quad H_2, \quad N_2, \quad A$$
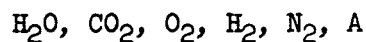
Mass conservation equations:

$$\sum_{J=1}^{6} X_J = 1 \tag{1}$$

$$X_A = C_1(2X_{N_2}) \tag{2}$$

$$2X_{N_2} = C_2(2X_{CO_2} + X_{H_2O} + 2X_{O_2}) \tag{3}$$

$$X_{CO_2} = C_3(2X_{CO_2} + X_{H_2O} + 2X_{O_2})$$ (4)

$$2X_{H_2} + 2X_{H_2O} = C_4(2X_{CO_2} + X_{H_2O} + 2X_{O_2})$$ (5)

For $1.0 > R_{eq} \geq 0$

$$X_{H_2} = 0, \quad X_J = X_J(R_{ch}, R_{eq})$$

For $R_{eq} = 1$

$$X_{H_2} = 0, \quad X_{O_2} = 0, \quad X_J = X_J(R_{ch})$$

For the hydrogen-air case $(R_{ch} = 0) \quad R_{eq} > 1$

$$X_{O_2} = 0, \quad X_J = X_J(R_{eq})$$

consider the following reaction:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$
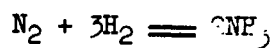
Equilibrium expression

$$P_{lim}^2 = \frac{X_{NH_3}^2}{K_{10}^2} X_{H_2}^3 X_{N_2}$$

for

$$X_{NH_3} > 0.01, \quad P > P_{lim}$$

Thermodynamic properties of gas mixtures.- The previous deriva-
tions have outlined the solution for gas mixture composition. With the
chemical composition defined and a tabulation of the thermodynamic
properties of the pure constituents provided, the thermodynamic properties
of a gas mixture can be calculated by the following (Ref. 6):

Enthalpy:
$$H = \frac{R}{M} \Sigma_J X_J \frac{H^O_J}{R}$$

Entropy:
$$S = \frac{R}{M} \Sigma_J X_J \left(\frac{S^O_J}{R} - \ln P - \ln X_J \right)$$

Mean Molecular Weight: $M = \Sigma_J X_J M_J$

where $\frac{H^O_J}{R}$ and $\frac{S^O_J}{R}$ are the thermodynamic properties of the pure
constituents at reference pressure (1 atmosphere). The thermodynamic
expressions above inherently assume that the pure constituents obey the
perfect gas law.

The standard reference state of the elements A, N, O, H, C are
taken from Reference 6, that is:

$$
\begin{array}{lll}
A & as & A \\
N & as & N_2 \\
O & as & O_2 \\
H & as & H_2 \\
C & as & C \text{ (solid)}
\end{array}
$$

By definition, the energy content of these elements in their standard reference states $(T = 0^\circ R)$ is zero. Equations for the computation of fuel enthalpies consistent with this thermodynamic basis are presented in Reference 7.

A listing of the computer program to calculate the composition and thermodynamic properties of this gas model is presented and discussed in the Appendix. Computational time for this program has been estimated at 6000 cases/min on the IBM 7094 data processing system at the Langley Research Center. One case is defined as the computation of one point on a Mollier Diagram.

CHAPTER III

RESULTS AND DISCUSSION

Comparison of gas models.- The computer program for the simplified

combustion gas model has been used to calculate the thermodynamic

properties of the stoichiometric kerosene-air and hydrogen-air systems.

The purpose of this calculation is to compare the results of the simpli-

fied gas model with the more extensive treatments of References 6 and 7.

Since the thermodynamic properties of the pure constituents used in the

simplified model were taken from these references, the differences

between the results of the simplified model and the reference models

are due to the formation of the neglected chemical species N, NH, NH_3,

NO.

Figure 3 is a Mollier diagram for the stoichiometric products of

combustion of kerosene with air $(R_{ch} = 0.5)$. The solid curves are

values plotted from the tabulated data of Reference 7. The dashed

curves are values obtained from the computer program for the simplified

model. Unfortunately, the data presented in Reference 7 are limited to

temperatures below 5000° R. Since the formation of species includi..3

atomic nitrogen (N, NH, NH_3) is more important at temperatures ab ve

5000° R, the good agreement between gas models is not surprising.

Figure 4 is a Mollier diagram for the stoichiometric products of

combustion of hydrogen with air $(R_{ch} = 0)$. The solid curves are values

plotted from the tabulated data of Reference 6. The dashed curves are

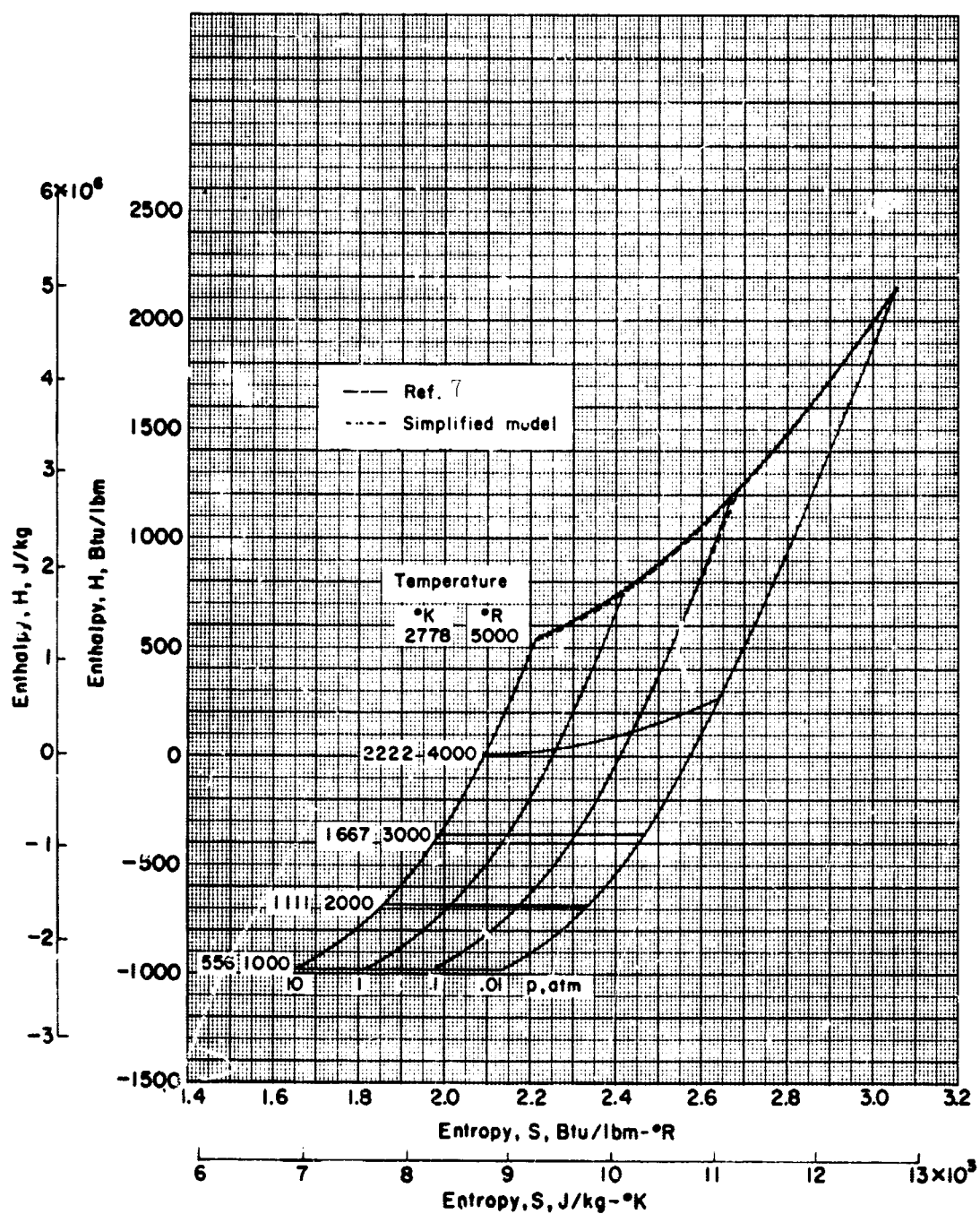values obtained from the computer program for the simplified model.

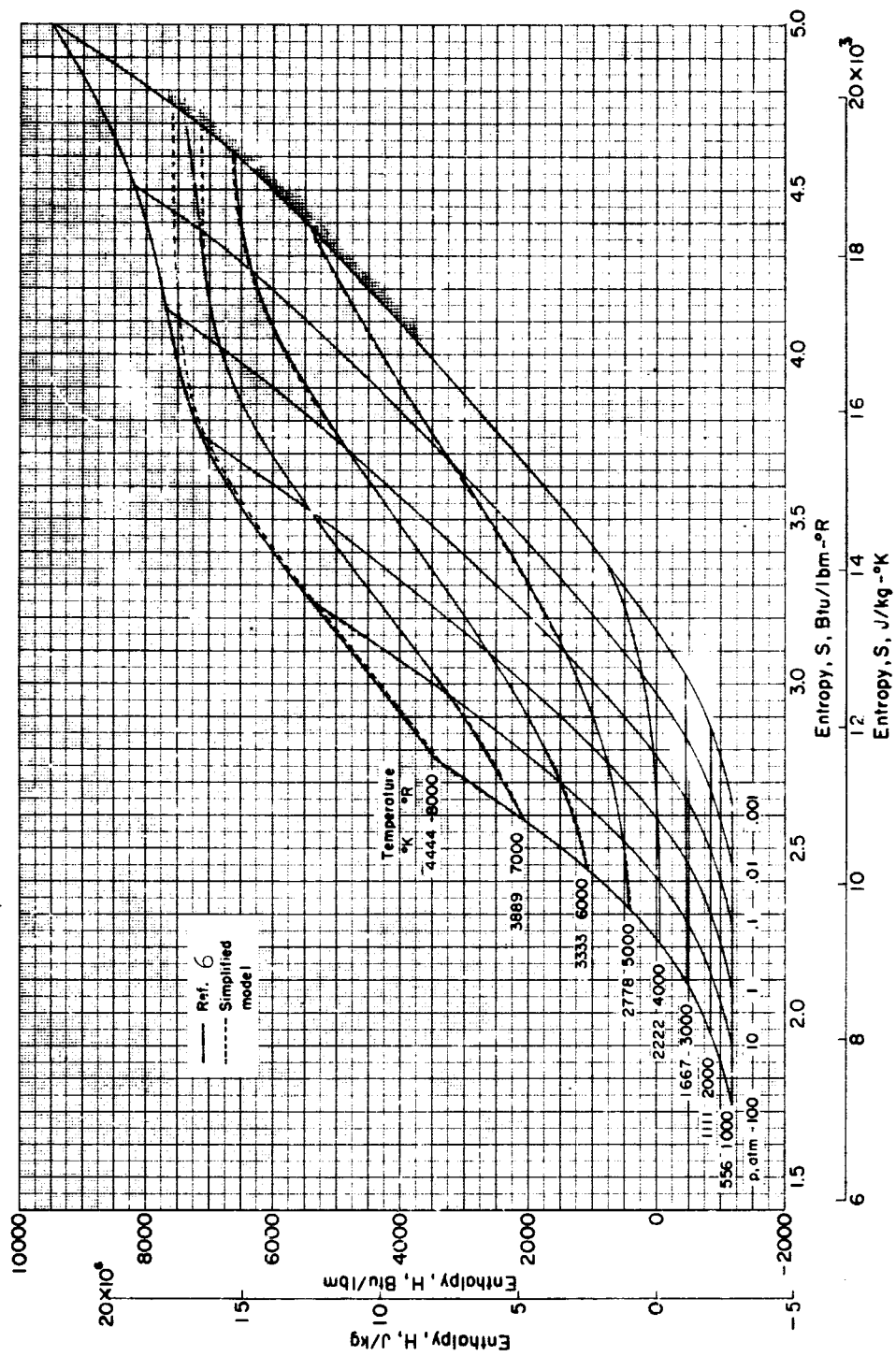Figure 3.- Mollier diagram; kerosene-air combustion products $(R_{ch} = 0.5)$, $R_{eq} = 1.0$.

Figure 4.- Mollier diagram; hydrogen-air combustion products ($R_{ch} = 0$), $R_{eq} = 1.0$.

27

The thermodynamic properties tabulated in Reference 6 cover temperatures as high as 10,000° R. The substantial disagreement above 7000° R at low pressures is due to the formation of atomic nitrogen species. An interesting result is that the agreement between lines of constant pressure is much better than the agreement between lines of constant temperature. This result is fortunate, since, for thermodynamic processes such as isentropic nozzle expansion, temperature is not used directly to calculate performance.

The simultaneous conditions of high temperatures and low pressures, the area of substantial disagreement between the simplified gas model and the reference gas models, are beyond the realm of operation of typical hypersonic engine cycles. For example, for subsonic combustion ramjets, combustion pressures and temperatures are high since the airstream is brought nearly to stagnation conditions before combustion. For super-sonic combustion ramjets, combustion pressures and temperatures are low, since a large portion of the total air enthalpy remains in the form of kinetic energy. Hence, the conditions of high temperatures and low pressures do not occur simultaneously for engine cycles currently considered feasible for hypersonic flight.

Ramjet performance comparison.- In applying the simplified gas model to hypersonic engine calculations, it is of interest to determine the effect which the use of the simplified gas model has on the calculated performance of a typical subsonic combustion ramjet.

The subsonic combustion ramjet is perhaps the simplest air-breathing engine cycle. Referring to the sketch below, the free-stream

air is decelerated through an air intake or inlet to low subsonic speeds in the burner. Here fuel is added at low velocity, combustion takes place, and then the flow is accelerated through a nozzle.
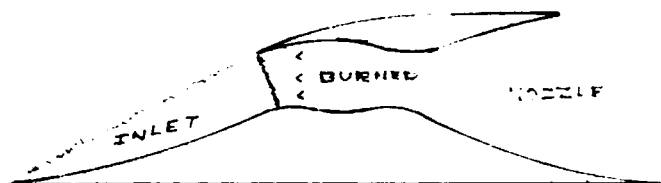
Since the purpose of this performance calculation is to show the effect of small differences in thermodynamic properties on ramjet performance, the following simplifying assumptions were made:

1. Free-stream Mach number chosen along a constant dynamic pressure path (q = 1500 psf).

2. Airstream decelerated to stagnation conditions with total pressure recovery degraded to 10 atmospheres. (A good assumption at high Mach numbers, due to internal duct pressure limitations.)

3. Completely mixed stoichiometric hydrogen-air combustion.

4. No pressure losses during combustion (Pt_{nozzle} = 10 atmospheres).

5. Enthalpy of injected hydrogen equals zero. Molecular hydrogen is a reference element, thus $H^o_{H_2}$ = 0 at T = 0° R.

6. Combustion gas is isentropically expanded to free stream, ...tic conditions using so-called "shifting equilibrium."

The 1962 standard atmosphere (Ref. 10) yields free-stream static conditions, and together with assumption (1) gives the variation of altitude with Mach number shown in Figure 5. For steady adiabatic flow, the total energy in the airstream is given by:

$$H_{t,air} = H_{\infty,air} + \frac{V_{\infty}^2}{2Jg}$$

For an adiabatic combustion process:

$$H_{t_{products}} = \frac{H_{t_{air}} + fH_{t_{hydrogen}}}{1 + f}$$

With two properties $\left(H_{t_{products}}, P_{t_{nozzle}}\right)$ of the combustion gas defined, the Mollier diagram can be entered. Figure 6 is a schematic of a Mollier diagram showing lines of constant pressure for the simplified gas model and that of Reference 6. Since the simplified gas model neglects the dissociated nitrogen species, the entropy level is slightly less than that obtained from Reference 6. In expanding the combustion gas to free-stream static pressure, the gas enters the region of almost exact agreement between gas models. Consequently, the expansion using the simplified gas model gives a slightly larger value of $H_t - H_s$ than Reference 6. However, the effect of the difference in ΔH is reduced by the fact that:

$$V_j \sim \sqrt{H_t - H_s}$$
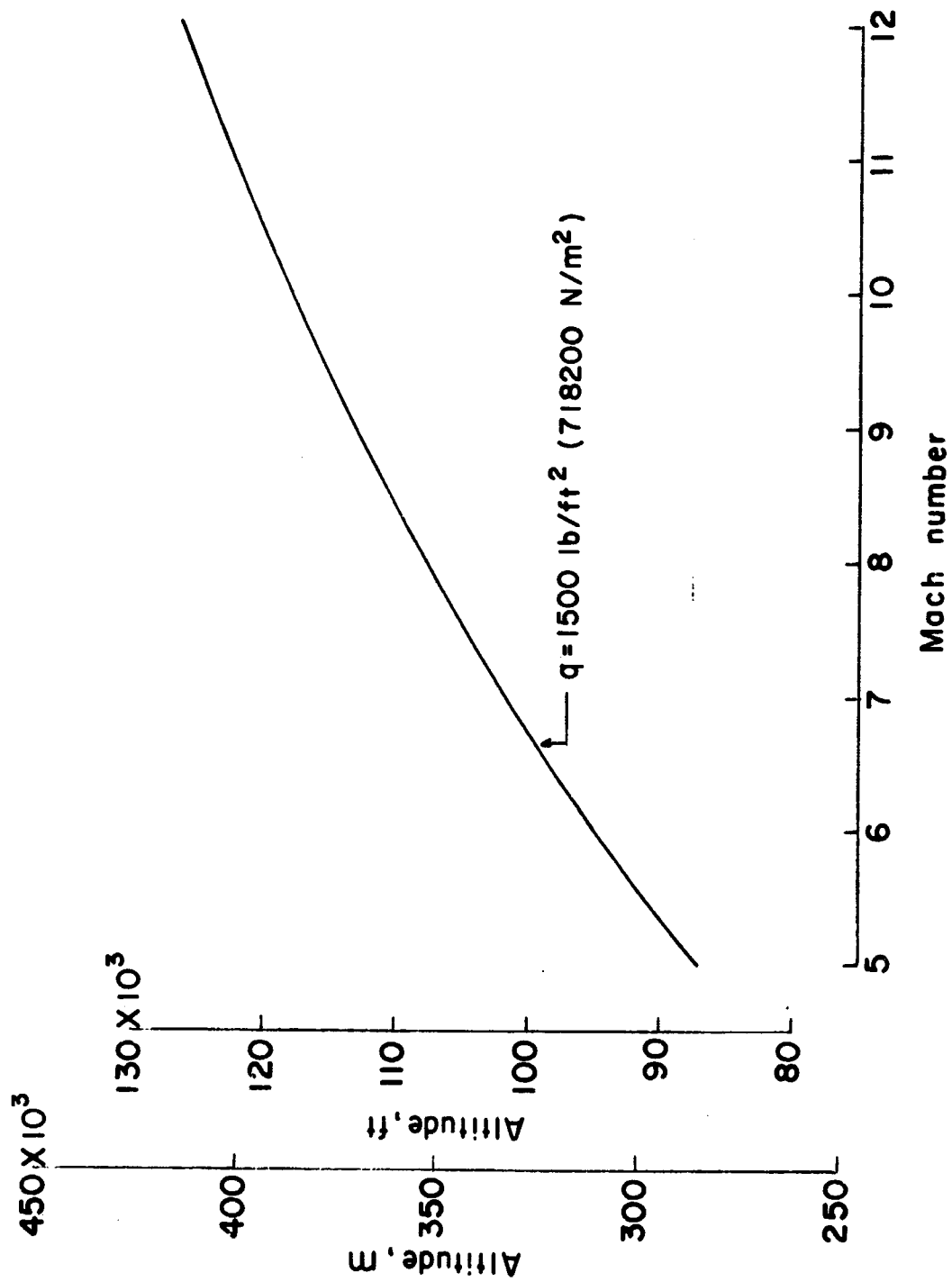
Figure 5.- Assumed flight profile for ramjet performance calculation.

COMPUTER PROGRAM

The calculation procedure for determining gas composition and thermodynamic properties for the simplified gas model has been programed for and computed on the IBM 7094 data processing system at the Langley Research Center. A printout of the program is presented in this appendix. The program is written in Fortran language (Ref. 10). The sumbols used for the program are as follows:

RCH	R_{ch}	X(1)	X_{H_2O}
REQ	R_{eq}	X(2)	X_{CO_2}
TEMP	T	X(3)	X_{O_2}
P	P	X(4)	X_{H_2}
M	M	X(5)	X_{N_2}
H	H	X(6)	X_A
S	S	X(7)	X_O
MT(J)	M_J	X(8)	X_H
TT(I)	T_I	X(9)	X_{CO}
HT(I,J)	H_J^o	X(10)	X_{OH}
ST(I,J)	S_J^o	X(11)	X_{NO}
		X(12)	X_N

Input.- The input is read into the IBM 7094 data processing system by the Fortran statement:

READ (5,100) RCH,REQ,TEMP,P
100 FORMAT (4E 16.8)

For example, an input card would be:

Col.- 1   17   23   49

    +0.00000000E+00   +0.10000000E+01   +0.50000000E+04   +0.10000000E+00

        Output.- The output for this program is the mole fractions of

each constituent and the thermodynamic properties of the gas mixture.

For example, output for the case above would be:

RCH=0.00000000E-38 REQ=0.10000000E+01 TEMP=0.50000000E 04R P=0.100000000E 00ATM

XH2O	XCO2	XO2	XH2
0.18315569E 00	0.00000000E-38	0.27084661E-01	0.71114589E-01

XN2	XA	XO	
0.57613321E 00	0.71005768E-02	0.25695777E-01	0.63610586E-01

XCO	XOH	XNO	XN
0.00000000E-38	0.46109576E-01	0.00000000E-38	0.00000000E-38

N=0.21993865E 02   H=0.14316146E   04BTU/LBM S=0.30918686E 01BTU/LBM-

        Built-in data.- The thermodynamic properties of the pure constit-
uents $\left(\dfrac{H_J^0}{R}, \dfrac{S_J^0}{R}\right)$ are taken from References 6 and 7 and input as two-
dimensional arrays named:

                HT(I,J) and ST(I,J)

Where "I" is the index on temperature and "J" is the index on constit-
uents. The thermodynamic properties are input for the discrete

temperatures given in TT(I). The enthalpy array HT(I,J) is interpolated linearly while the entropy array ST(I,J) is interpolated logarithmically.

Complete program.- The following program has been used on the IBM 7094 data processing system at the Langley Research Center.

```
C      THERMODYNAMIC PROPERTIES OF HYDROCARBON-AIR COMBUSTION PRODUCTS
C H2O  CO2   O2   H2   N2   A    O    H   CO   OH   NO    N
C X(1) X(2) X(3) X(4) X(5) X(6) X(7) X(8) X(9) X(10) X(11) X(12)
       DIMENSION TT(16),MT(12),HT(16,12),ST(16,12),X(12),Y(99),F(99),
      1Z(99),TY(99)
       REAL M,MT,K1,K2,K3,K4,K5,K6,K7,K8,K9,K10
C
C THERMODYNAMIC PROPERTIES OF PURE CONSTITUENTS
C
       DATA(MT(J),J=1,12)/18.016,44.01,32.00,2.016,28.016,
      139.944,16.00,1.008,28.01,17.008,30.008,14.008/
       DATA(TT(I),I=1,16)/0.,200.,400.,600.,800.,1000.,1300.,1600.,2000.,
      12500.,3000.,3500.,4000.,5000.,6000.,7000./
       DATA((HT(I,J),I=1,16),J=1,5)/-51727.,-51100.,-50400.,-49700.,
      1-48900.,-47743.,-46297.,-44939.,-42944.,-40290.,-37449.,-34456.,
      2-31354.,-24889.,-18176.,-11296.,-85117.,-84000.,-83500.,-82801.,
      3-81818.,-80746.,-79007.,-77147.,-74535.,-71116.,-67595.,-63983.,
      4-60312.,-52857.,-44500.,-37000.,0.,698.,1400.,2104.,2826.,3574.,
      54744.,5963.,7639.,9794.,11996.,14241.,16524.,21203.,26021.,30953.,
      60.,751.,1356.,2052.,2755.,3458.,4518.,5588.,7042.,8918.,10867.,
      712886.,14964.,19272.,23744.,28355.,0.,699.,1398.,2099.,2801.,
      83513.,4608.,5743.,7316.,9356.,11456.,13597.,
      915768.,20171.,24629.,29124./
       DATA((HT(I,J),I=1,16),J=6,9)/0.,500.,1000.,1500.,2000.,2500.,
```

13250.,4000.,5000.,6250.,7500.,8750.,10000.,12500.,15000.,17500.,

253425.,54000.,54436.,54900.,55345.,56165.,56801.,57600.,58594.,

359855.,61110.,62356.,63612.,66120.,68640.,71183.,46759.,47300.,

447712.,48360.,48679.,49336.,49977.,50763.,51752.,53008.,54261.,

555503.,56756.,59255.,61758.,64357.,-24639.,-24000.,-23000.,

6-22540.,-21835.,-21116.,-20009.,-18856.,-17261.,-15193.,-13073.,

7-10912.,-8725.,-4295.,0.,3500./

  DATA((HT(I,J),I=1,16),J=10,12)/8424.9,9098.,9750.,10455.,11222.,

111997.,13043.,14130.,15605.,17520.,19508.,21558.,23664.,27996.,

232456.,37024.,19455.,20006.,20567.,21427.,22220.,23091.,24248.,

325445.,26992.,29185.,31341.,33580.,35743.,40220.,44741.,49302.,

4101922.,102000.,102000.,102156.,103312.,104590.,105104.,105933.,

5106908.,108173.,109422.,110663.,111916.,114425.,116946.,119518./

  DATA((ST(I,J),I=1,16),J=1,4)/0.,18.68,21.55,23.167,24.338,25.273,

126.434,27.400,28.505,29.691,30.725,31.6464,32.4745,33.9163,35.13,

236.2003,0.,21.700,24.550,26.20115,27.61677,28.61060,30.32729,

331.61326,33.06995,34.59469,35.87841,36.98959,37.97139,39.63861,

441.0,42.19,0.,21.1538,23.6633,25.0721,26.1033,26.9292,27.9544,

528.7966,29.7306,30.6915,31.4947,32.1868,32.796,33.8396,34.7178,

635.4778,0.,12.5375,14.7172,16.1042,17.1073,17.8829,18.8146,19.35,

720.3628,21.2011,21.9103,22.5326,23.0880,24.0484,24.8623,25.5747/

  DATA((ST(I,J),I=1,16),J=5,9)/0.,19.5245,22.0313,23.4305,24.4362,

125.2221,26.1808,26.9656,27.8431,28.7524,29.5175,30.1789,30.758,

```
C
C GAS MODEL CONSTANTS
C
      C=4.773384
      C1=.00616227
      C2=3.727445
      C3=(2.*REO*RCH)/(1.+4.*RCH)
      C4=(2.*REO)/(1.+4.*RCH)
      IF(TEMP.GT.(100.*ALOG10(P)+2800.))GO TO 1.
    7 IF(REO.EQ.1.)GO TO 2
      IF(REO.GT.1.)GO TO 3
C
C NON-DISSOCIATING GAS MODEL, REQ.LT.1
C
      X(1)=(2.*C4)/(C4+2.*C)
      X(2)=(4.*C3)/(C4+2.*C)
      X(3)=(2.-4.*C3-C4)/(C4+2.*C)
      X(5)=(2.*C2)/(C4+2.*C)
      X(6)=(4.*C2*C1)/(C4+2.*C)
      GO TO 50
C
C NON-DISSOCIATING GAS MODEL, REQ.EQ.1
C
```

```
     231.74,32.55,33,25,0.,16.11,17.90,18.90,19.61,20.16,20.82,
     321.341,21.699,22.457,22.912,23.296,23.632,24.190,24.646,25.031,0.,
     416.59,18.61,19.662,20.401,16.965,21.632,22.156,22.7177,23.2772,
     523.7344,24.1205,24.4557,25.015,25.474,25.866,0.,11.280,13.08,14.,
     614.787,15.39,15.996,16.514,17.0724,17.6301,18.087,18.4713,18.81,
     719.3632,19.8195,20.2045,0.,20.39,22.80,24.19,25.21,26.007,26.98,
     827.773,28.66,29.59,30.36,31.02,31.61,32.60,33.45,34.15/
      DATA((ST(I,J),I=1,16),J=10,12)/0.,19.643,21.2024,22.4669,23.5156,
     124.300,25.234,25.9813,26.8053,27.6588,28.3836,29.0155,29.5779,
     230.54,31.36,32.06,0.,21.62,24.31,25.75,26.71,27.52,
     328.5805,29.397,30.269,31.250,32.036,32.7121,33.3028,34.3009,
     435.1249,35.8281,0.,15.92,17.71,18.71,19.43,19.979,20.638,21.155,
     521.713,22.272,22.727,23.1126,23.4466,24.0055,24.4654,24.8616/
C
C INPUT
C
  500 READ(5,100)RCH,REQ,TEMP,P
  100 FORMAT(4E16.8)
      WRITE (6,300) RCH,REQ,TEMP,P
  300 FORMAT(10X4HRCH=E15.8,4X4HREQ=E15.8,4X5HTEMP=E15.8,1HR,
     14X2HP=E15.8,3HATM)
      DO 12 J=1,12
   12 X(J)=0.
```

```
   2 X(1)=(2.*(1.-2.*C3))/(C+(1.-2.*C3))

     X(2)=(2.*C3)/(C+(1.-2.*C3))

     X(5)=C2/(C+(1.-2.*C3))

     X(6)=(2.*C2*C1)/(C+(1.-2.*C3))

     GO TO 50

   3 IF (RCH.EQ.0.)GO TO 14

     IF(REQ.GE.((1.+4.*RCH)/(2.*RCH)))GO TO 15

C

C NON-DISSOCIATING GAS MODEL, REQ.GT.1

C

     K8=10.**(1.747-(3415./TEMP))

     K9=10.**(9.272-(16210./TEMP))

     AA=(1.-K8)*(C+C4+2.*C3-1.)**2

     BB=(C-1.+C4+2.*C3)*(2.*(1.-2.*C3)+K8*(C4+6.*C3-2.))

     CC=K8*(2.-C4-4.*C3)*2.*C3

     X(9)=(SQRT(BB**2-4.*AA*CC)-BB)/(2.*AA)

     X(2)=(2.*C3/(C+C4+2.*C3-1.))-X(9)

     X(1)=((1.-2.*C3)*X(2)+(1.-C3)*X(9))/C3

     X(4)=X(1)*X(9)/(K8*X(2))

     X(5)=C2*(2.*X(2)+X(9)+X(1))/2.

     X(6)=2.*C1*X(5)

     PLIM=K9*X(2)/(X(9)**2)

     WRITE(6,200)PLIM
```

```
1 K1=10.**((89877./TEMP)-12.7295)

  K2=10.**((42367./TEMP)-6.2325)

  K3=10.**((47850./TEMP)-6.9570)

  K5=10.**((41612./TEMP)-5.8720)

  K6=10.**((90047./TEMP)-6.9505)

  K7=10.**((60437./TEMP)-6.2915)

  IF(REG.EQ.0.)GO TO 4

  IF(RCH.NE.0.) GO TO 5

  K4=0.

  GO TO 6

5 K4=10.**((50173./TEMP)-7.8785)

6 A22=P**3*K1*K4*(1.-2.*C3+C)

  A21=P**2*(K1*(1.+C)+2.*K2*K4*(1.-2.*C3))

  A20=2.*P*K2*(1.-C3)

  A12=P**2*K4*K5*(1.-2.*C3+C)

  A11=P*K-4(1.+C)+2.*K4*(1.-2.*C3))

  A10=2.*(1.-C3)

  A03=2.*P**2*C*K3*K4

  A02=P*(K4*(1.-2.*C3+C)+2.*K3*(C3+C))

  A01=1.+C-2.*P*K4*(1.-2.*C3)

  A00=2.*(C3-1.)

  B22=P**3*K1*K4*(2.-4.*C3-C4)

  B21=P**2*(K1*(2.-2.*C3-C4)+2.*K2*K4*(1.-2.*C3))
```

```
      B20=2.*P*K2*(1.-C3)

      B12=P**2*K4*K5*(1.-2.*C3-C4)

      B11=P*(K5*(1.-C3-C4)+K4*(1.-2.*C3))

      B10=1.-C3

      B03=2.*C4*P**2*K3*K4

      B02=C4*P*(2.*K3+K4)

      B01=C4

C
C ITERATION FOR CHEMICAL COMPOSITION
C
   21 Y(1)=(-1.*SQRT((1.+C)**2+16.*C*P*K3)-(1.+C))/(4.*C*P*K3)

      L=1

      IF(REQ.GT.1.)GO TO 25

   16 B=(Y(L)*(Y(L)*B12+B11)+B10)**2+4.*(Y(L)*(Y(L)*B22+B21)+B20)*(Y(L)
     1*(Y(L)*(Y(L)*B03+B02)+B01))

      IF(B.LT.0.)GO TO 20

      Z(L)=(SQRT(B)-1.*(Y(L)*(Y(L)*B12+B11)+B10))/((Y(L)*(Y(L)*B22+B21)
     1+B20)*2.)

      IF((Y(L).LT..00001).AND.(REQ.LE.1.))GO TO 7

      F(L)=Z(L)*(Z(L)*(Y(L)*(Y(L)*A22+A21)+A20)-(Y(L)*(Y(L)*A12+A11)+
     1A10))+(Y(L)*(Y(L)*(Y(L)*A03+A02)+A01)+A00)

      IF((F(L).GT.-.0001).AND.(F(L).LT..0001))GO TO 8

      DELF=(Z(L)**2)*(2.*A22*Y(L)+A21)+Z(L)*(2.*A12*Y(L)+A11)+3.*A03*
     1Y(L)**2+2.*A02*Y(L)+A01-(2.*(Y(L)*(Y(L)*A22+A21)+A20)*Z(L)+(Y(L)
     2*(Y(L)*A12+A11)+A10))*((Z(L)**2)*(2.*B22*Y(L)+B21)+Z(L)*(2.*B12
     3*Y(L)+B11)-(3.*B03*Y(L)**2+2.*B02*Y(L)+B01))/(2.*(Y(L)*(Y(L)*B22
     4+B21)+B20)*Z(L)+(Y(L)*(Y(L)*B12+B11)+B10))
```

```
      Y(L+1)=Y(L)-F(L)/ABS(DELF)

      L=L+1

      GO TO 16

   20 Y(L)=.1*Y(L)

      IF((Y(L).LT..00001).AND.(REQ.LE.1.))GO TO 7

      GO TO 16

   25 Z(1)=(+1.*SQRT((2.*C4*(1.-C3)+1.+C)**2+16.*P*K2*C4*(1.-C3)*(C4*(1.
     1-C3)+1.+C))-(2.*C4*(1.-C3)+1.+C))/(4.*P*K2*(C4*(1.-C3)+1.+C))

   28 B=(B21*Z(L)**2+B11*Z(L)-B01)**  -4.*(B20*Z(L)**2+B10*Z(L))*(B22
     1*Z(L)**2+B12*Z(L)-B02)

      K=1

      TY(K)=(-1.*SQRT(B)-(B21*Z(L)**2+B11*Z(L)-B01))/(2.*(B22*Z(L)**2
     1+B12*Z(L)-B02))

   27 DEL=(B22*TY(K)**2+B21*TY(K)+B20)*Z(L)**2+(B12*TY(K)**2+B11*TY(K)
     1+B10)*Z(L)-(B03*TY(K)**3+B02*TY(K)**2+B01*TY(K))

      TY(K+1)=TY(K)-DEL/(-3.*B03*TY(K)**2+2.*(B22*Z(L)**2+B12*Z(L)-B02)
     1*TY(K)+(B21*Z(L)**2+B11*Z(L)-B01))

      K=K+1

      GO TO 27

   26 Y(L)=TY(K)

      F(L)=Z(L)*(Z(L)*(Y(L)*(Y(L)*A22+A21)+A20)+(Y(L)*(Y(L)*A12+A11)+
     1A10))+(Y(L)*(Y(L)*(Y(L)*A03+A02)+A01)+A00)
```

```
      IF((F(L).LT..0001).AND.(F(L).GT.-.0001))GO TO 8

      IF(Z(L).LT..00001)GO TO 7

      IF(L.EQ.1)GO TO 29

      Z(L+1)=Z(L)-F(L)*(Z(L-1)-Z(L))/(F(L-1)-F(L))

      L=L+1

      GO TO 28

   29 Z(2)=.5*Z(1)

      L=2

      GO TO 28

    8 X(7)=Y(L)

      IF(REQ.EQ.0.)GO TO 22

      X(8)=Z(L)

      X(1)=P**2*K1*X(7)*X(8)**2

      X(3)=P*K3*X(7)**2

      X(10)=P*K5*X(7)*X(8)

      X(9)=(C3*(X(1)+2.*X(3)+X(7)+X(10)))/((1.-2.*C3)*P*K4*X(7)+1.-C3)

      X(2)=P*K4*X(7)*X(9)

      X(4)=P*K2*X(8)**2

      X(5)=(C2/2.)*(2.*X(2)+X(1)+2.*X(3)+X(7)+X(9)+X(10))

      X(6)=2.*C1*X(5)

      GO TO 50

    C
```

```
C DISSOCIATING AIR
C
    4 A22=0.
      A21=0.
      A20=P*K6*(1.+2.*C1)
      A12=0.
      A11=P*K7*(1.+C1)
      A10=1.+C1
      A03=0.
      A02=P*K3
      A01=1.
      A00=-1.
      B22=0.
      B21=0.
      B20=2.*P*K6
      B12=0.
      B11=P*K7*(1.-C2)
      B10=1.
      B03=0.
      B02=2.*P*K3*C2
      B01=C2
      GO TO 21
   22 X(10)=Z(L)
```

```
      X(11)=P*K7*X(7)*X(12)

      X(3)=P*K3*X(7)**2

      X(5)=(C2*(2.*X(3)+X(7)+X(11))-X(11)-X(12))/2.

      X(6)=C1*(2.*X(5)+X(11)+X(12))
C
C CALCULATION OF GAS MIXTURE THERMODYNAMIC     PERTIES
C
   50 DO 9 I=1,16

      IF(TEMP-TT(I))10,10,9

    9 CONTINUE

   10 DELH=(TEMP-TT(I-1))/(TT(I)-TT(I-1))

      DELS=(ALOG(TEMP/TT(I-1)))/(ALOG(TT(I)/TT(I-1)))

      M=0.

      H=0.

      S=0.

      DO 11 J=1,12

      IF(X(J).EQ.0.)GO TO 11

      M=M+X(J)*MT(J)

      H=H+X(J)*(HT(I-1,J)+(HT(I,J)-HT(I-1,J))*DELH)

      S=S+X(J)*(ST(I-1,J)+(ST(I,J)-ST(I-1,J))*DELS-ALOG(P*X(J)

   11 CONTINUE

      H=(1.98588/M)*H

      S=(1.98588/M)*S
```
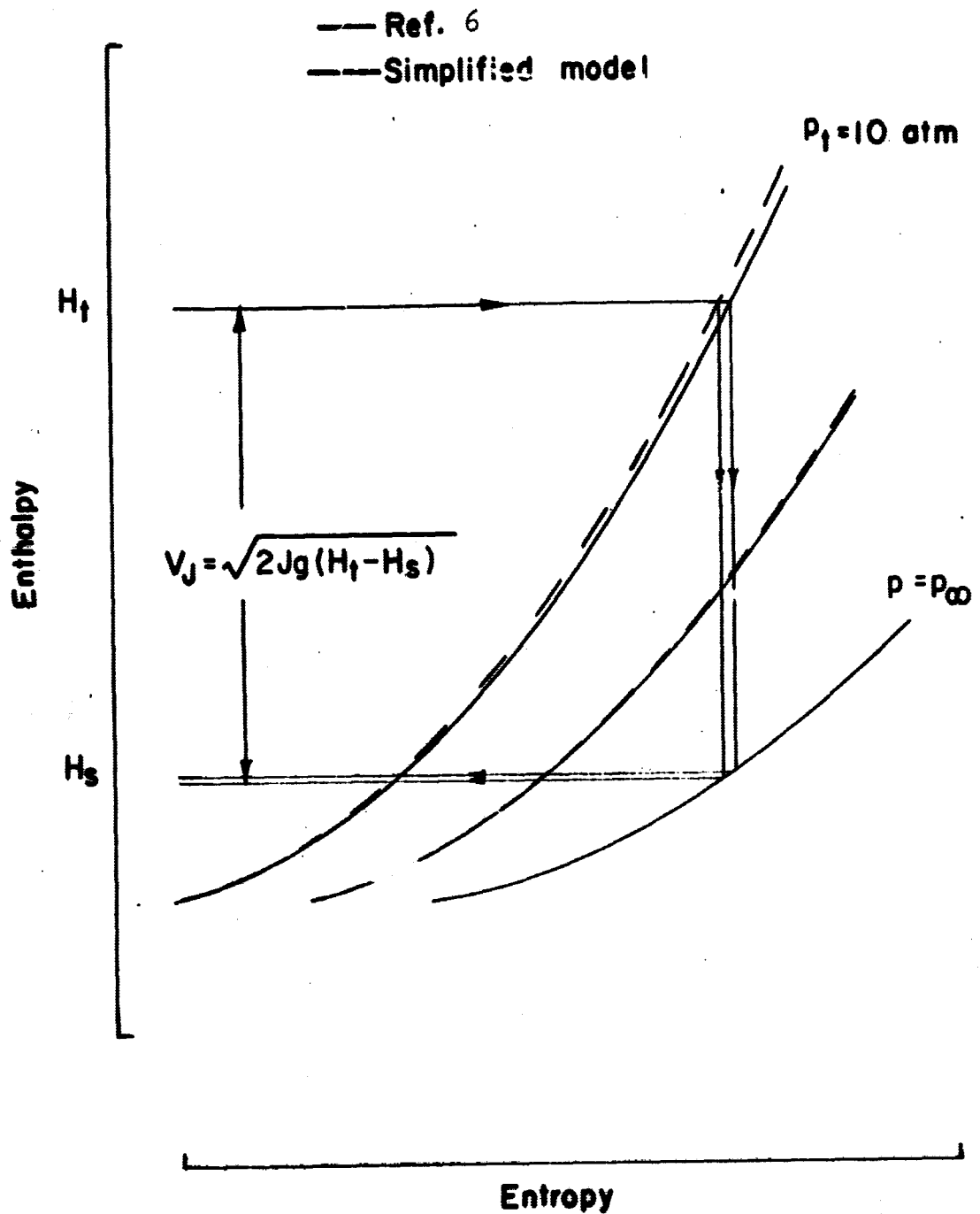
Figure 6.- Isentropic nozzle expansion process.

The performance parameters are given by the following expressions:

$$\frac{F_{net}}{W_A} = (1 + f)\frac{V_j}{g} - \frac{V_\infty}{g}$$

$$I_{SP} = \frac{\frac{F_{net}}{W_A}}{f}$$

The variation of specific impulse with Mach number for this idealized ramjet is presented in Figure 7. The solid curve was calculated using the thermodynamic properties of Reference 6. The dashed curve was calculated using the computer program for the simplified gas model. The maximum deviation is 1 per cent.

Summary of solid carbon and ammonia formation.- The formation of solid carbon extracts useful energy from the combustion gas. If this phenomenon occurs during a nozzle expansion process, the useful energy absorbed in forming solid carbon is not recoverable and a loss in performance results.

The derivation of the nondissociating $(T \leq T_{cut-off})$ fuel rich gas model required one chemical reaction in order that the formation of carbon monoxide (CO) could be included. The equilibrium expression resulting from the required reaction is independent of pressure. Consequently, the composition of the gas in this region is independent of pressure. This fact simplifies the treatment of solid
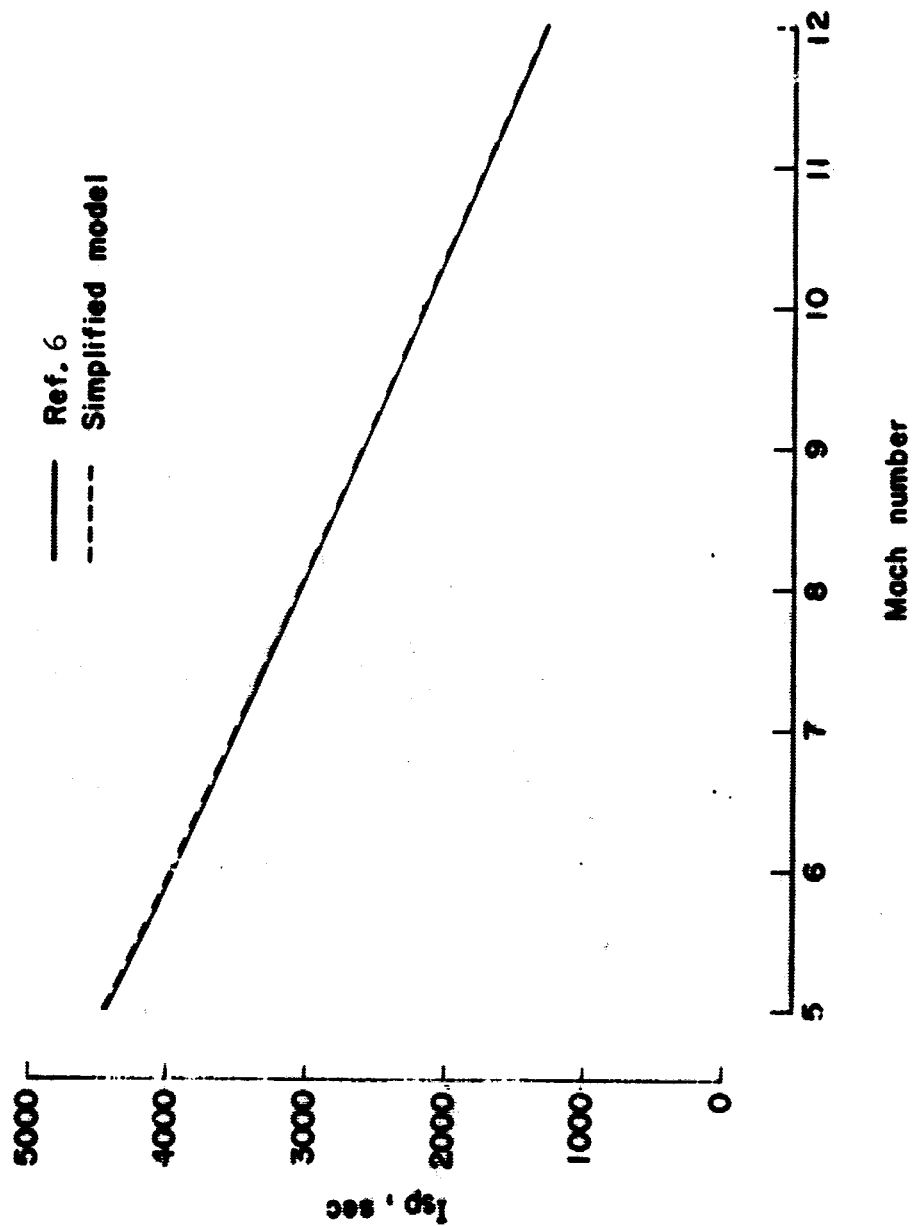
Figure 7.- Effect of gas model on typical ramjet performance. Hydrogen-air combustion, $R_{eq} = 1.0$, $q = 1500$ lb/ft^2, $P_t = 10$ atm; isentropic fully expanded nozzle; 1962 Standard Atmosphere.

carbon formation, since the limiting pressure above which solid carbon will form is related to temperature and composition only.

The computer program for the simplified gas model indicates the formation of solid carbon by an error statement. When the limiting pressure is exceeded, the error statement is printed, but the program computes the thermodynamic properties as though solid carbon had not formed. When the limiting equivalence ratio is exceeded, the error statement is printed and no calculations are made. The limiting pressure for solid carbon formation is readily extracted from the thermodynamic calculations. Figures 8 through 10 present the variation of limiting pressure with equivalence ratio and temperature for methane-air (R_{ch} = 0.25), kerosene-air (R_{ch} = 0.5), and benzene-air (R_{ch} = 1) combustion product, respectively. For all cases, as

$$R_{eq} \to R_{eq_{lim}} \qquad P_{lim} \to 0 \qquad \text{since} \qquad X_{CO_2} \to 0$$

$$R_{eq} \to 1 \qquad P_{lim} \to \infty \qquad \text{since} \qquad X_{CO} \to 0$$

The formation of ammonia is considered only for the hydrogen-air, nondissociating, fuel rich system. The composition of the gas under these conditions depends upon equivalence ratio only. Therefore, the limiting pressure above which the mole fraction of ammonia is greater than some arbitrary amount is related to temperature and composition.

The computer program for the simplified gas model indicates the formation of ammonia ($X_{NH_3} > 0.01$) by an error statement. When the limiting pressure is exceeded, the error statement is printed, but the
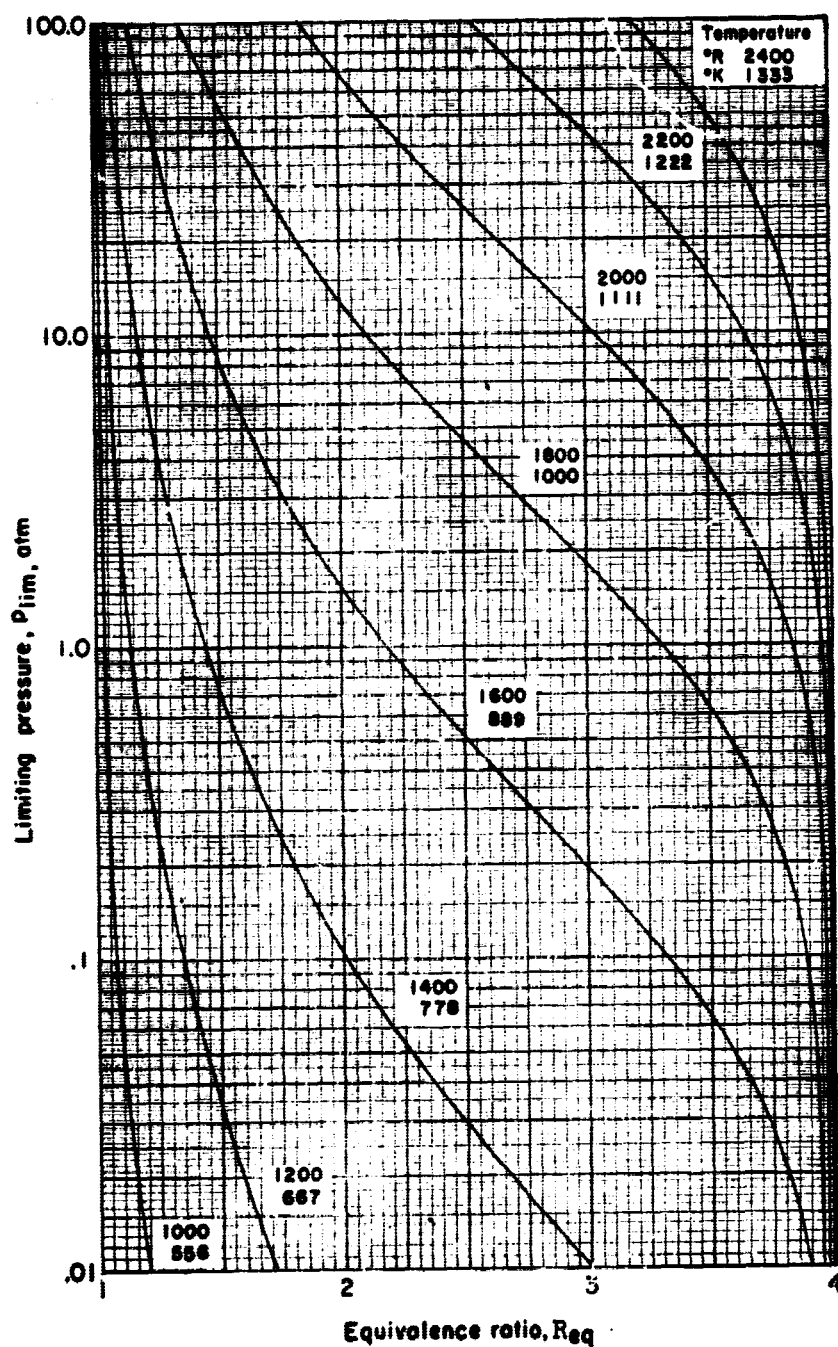
Figure 8.- Limiting pressure for solid carbon formation, methane-air combustion products (R_{ch} = 0.25), $R_{eq,lim}$ = 4.0.
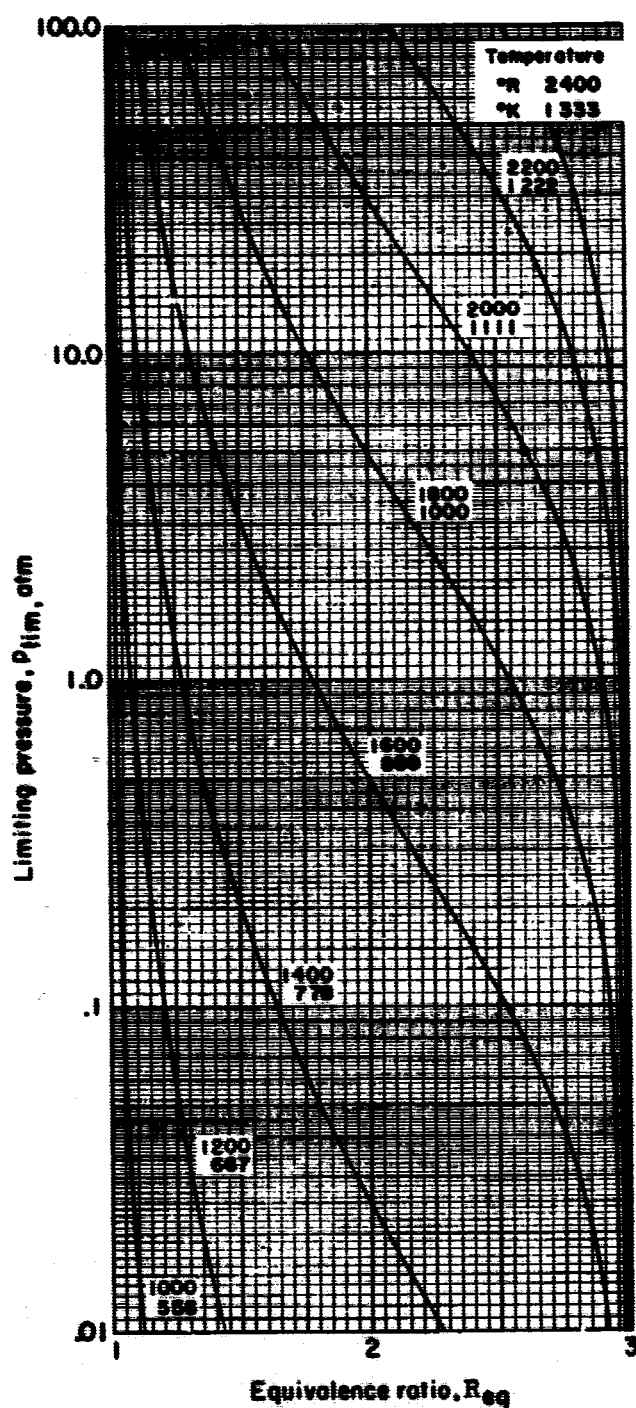
Figure 9.- Limiting pressure for solid carbon formation, kerosene-air combustion products (R_{ch} = 0.5), $R_{eq,lim}$ = 3.0.
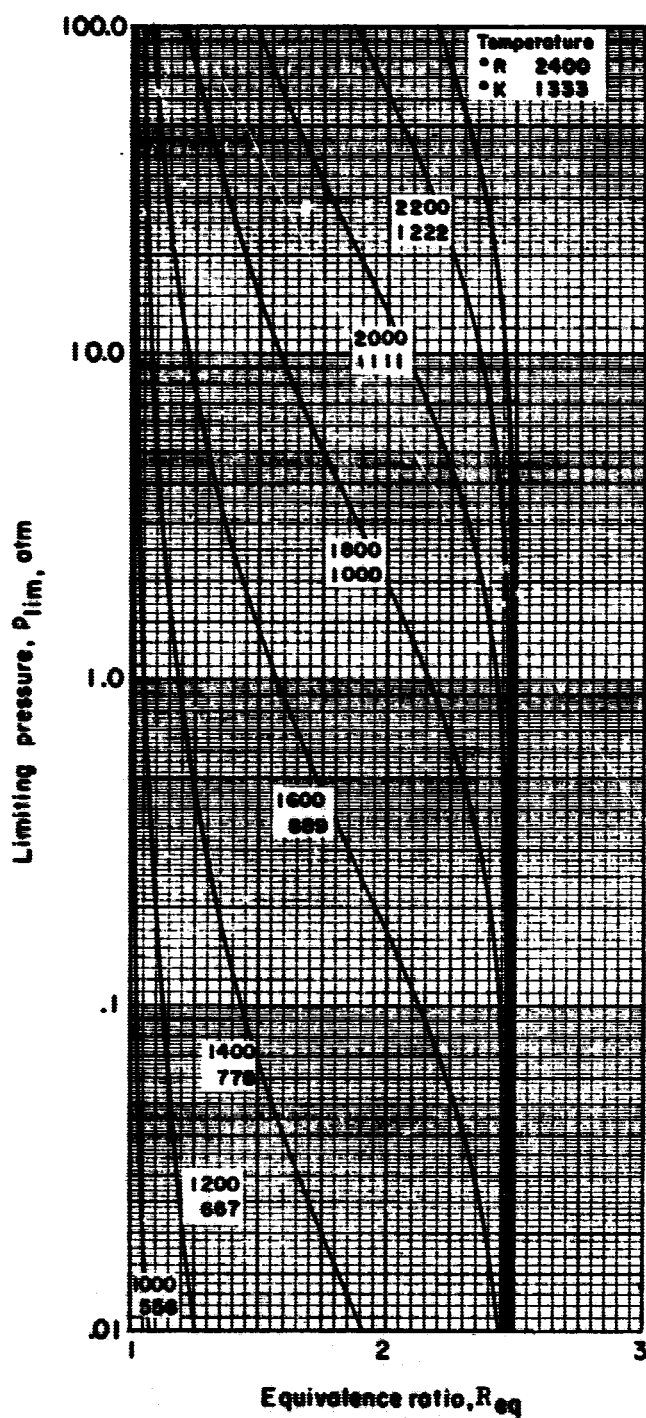
Figure 10.- Limiting pressure for solid carbon formation, benzene-air combustion products $(R_{ch} = 1.0)$, $R_{eq,lim} = 2.5$.

program computes the thermodynamic properties as though ammonia had not formed. Figure 11 presents the variation of limiting pressure with equivalence ratio and temperature for hydrogen-air combustion products. For all temperatures, as

$$R_{eq} \to \infty \qquad P_{lim} \to \infty \qquad \text{since} \qquad X_{N_2} \to 0$$

$$R_{eq} \to 1 \qquad P_{lim} \to \infty \qquad \text{since} \qquad X_{H_2} \to 0$$
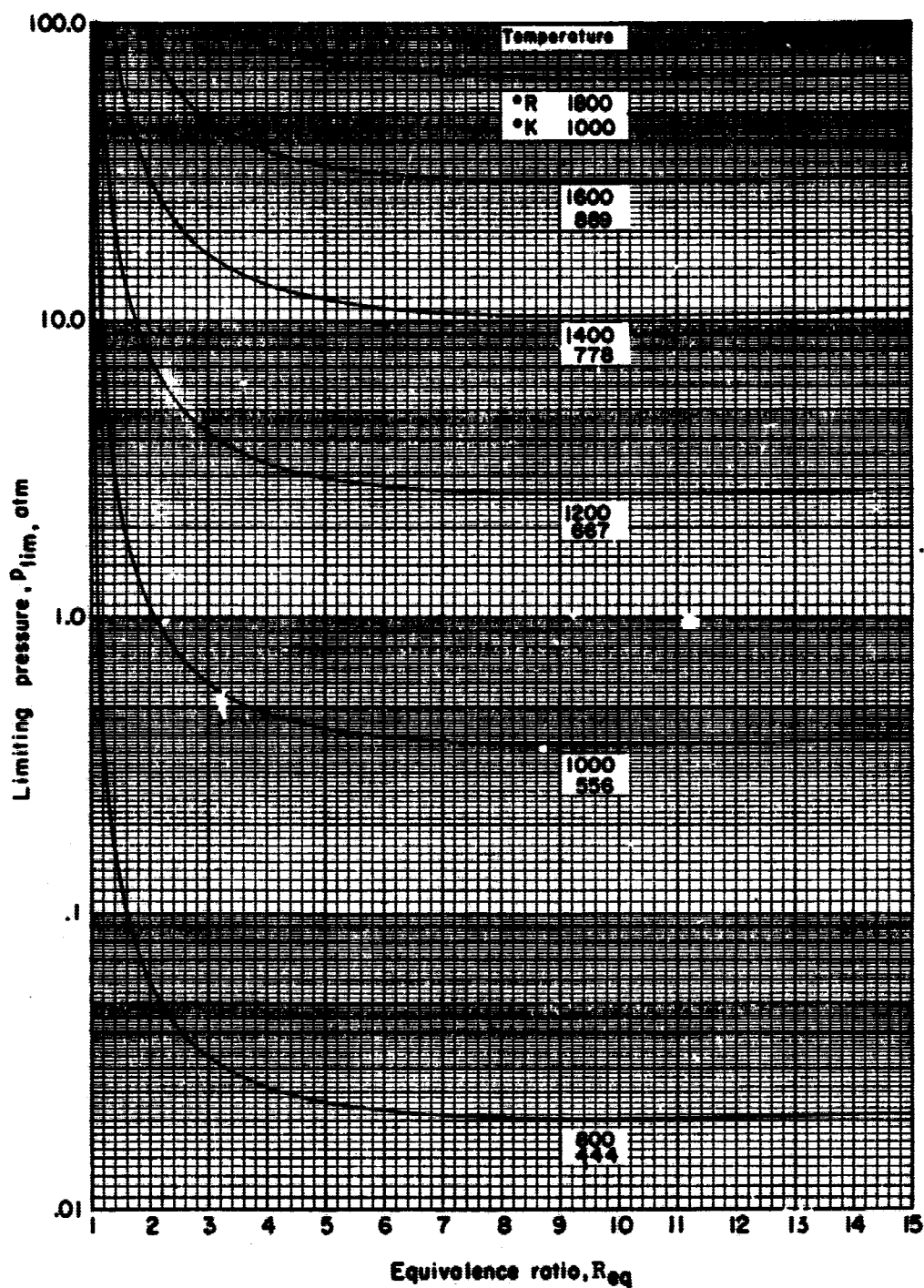
Figure 11.- Limiting pressure for ammonia formation (X_{NH_3} = 0.01), hydrogen-air combustion products (R_{ch} = 0).

CHAPTER IV

SUMMARY AND CONCLUSIONS

A simplified equilibrium hydrocarbon-air combustion gas model for convenient use in engine cycle computer programs has been presented. The generalized gas model presented includes the effects of dissociation and reduces to the special cases of hydrogen-air combustion products, as well as dissociating air. The associated computer program can be readily incorporated as a subroutine in a general engine cycle computer program or used alone to generate Mollier diagrams.

With the exception of pure air, this gas model neglects the formation of chemical species containing atomic nitrogen, which allows a considerable simplification of the solution for chemical composition. The effect of this assumption on the thermodynamic properties of stoichiometric kerosene-air and hydrogen-air combustion products is presented. The importance of this assumption is shown in terms of the performance of an idealized subsonic combustion ramjet. Good agreement between the simplified model and more comprehensive treatments is obtained in the range of temperatures applicable to hypersonic engine cycles.

The computer program has been used to calculate the limiting pressure for solid carbon and ammonia formation in fuel rich gas mixtures. The results of this calculation are presented as a function of temperature and equivalence ratio for the combustion products of various hydrocarbon fuels.

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REFERENCES

1. Zucrow, M. J.: Aircraft and Missile Propulsion. John Wiley and Sons, Inc., 1958.

2. Rothrock, A. M.: Turbojet Propulsion - System Research and the Resulting Effects on Airplane Performance. NACA RM 54H23, 1955.

3. Ferri, A.: Review of Problems in Application of Supersonic Combustion. Seventh Lanchester Memorial Lecture. Journal of the Royal Aeronautical Society, vol. 68, no. 645, Sept. 1964.

4. Hall, E. W.; Weber, R. J.: Tables and Charts for Thermodynamic Calculations Involving Air and Fuels Containing Boron, Carbon, Hydrogen, and Oxygen. NACA RM E56B27, 1956.

5. Clarke, J. F.; and McCheshey, M.: The Dynamics of Real Gases. Butterworth and Company, 1964.

6. Brown, W. G.; and Warlick, D. L.: Properties of Combustion Gases - System H_2 - Air. General Electric Company, Sept. 1964.

7. Fremont, H. A.: Properties of Combustion Gases - System $C_N H_{2N}$ - Air. General Electric Company, 1955.

8. Erickson, W. D.; Kemper, J. T.; and Allison, D. O.: A Method For Computing Chemical Compositions of Reacting-Gas Mixtures By Reduction to a Single Iteration Equation. NASA TN D-3488, 1966.

9. Zeleznik, F. J.; and Gordon, S.: An Analytical Investigation of Three General Methods of Calculating Chemical-Equilibrium Compositions. NASA TN D-473, 1960.

10. U.S. Standard Atmosphere, 1962.

11. McCracken, Daniel D.: A Guide to Fortran Programming. John Wiley
    and Sons, Inc., C. 1961.